

Exam in theory of extended systems (*part 2*)

March 2019

one-hour exam

Neither documents nor calculators are allowed.

The grading scale might be changed.

1. Questions on the lecture material (6 points)

- a) [**3 pts**] Bloch's theorem is usually explained in the particular case of one-electron systems. How would you apply Bloch's theorem to a system made of many *non-interacting* electrons? Would the same procedure be exact if we were considering (real) *interacting* electrons instead? If not, would it be possible to return exactly to a one-electron picture even though we describe interacting electrons? How?
- b) [**3 pts**] Do we need to know the non-interacting kinetic energy density functional for performing a practical Kohn–Sham density-functional theory (KS-DFT) calculation? What are the different strategies that can be adopted for developing density-functional approximations in KS-DFT?

2. Problem: Ionization potential in density-functional theory (16 points)

Let us consider both interacting ($\lambda = 1$) and non-interacting ($\lambda = 0$) \mathcal{N} -electron systems where \mathcal{N} is either equal to N (the system is then referred to as *neutral*) or $N - 1$ (it is then referred to as *ionized*). Their normalized ground-state wavefunctions $\Psi_{\mathcal{N}}^{\lambda,\xi}$ fulfill the following Schrödinger-like equation,

$$\left(\hat{T} + \lambda \hat{W}_{ee} + \sum_{i=1}^{\mathcal{N}} v^{\lambda,\xi}(\mathbf{r}_i) \times \right) \Psi_{\mathcal{N}}^{\lambda,\xi} = E_{\mathcal{N}}^{\lambda,\xi} \Psi_{\mathcal{N}}^{\lambda,\xi}, \quad \text{with } \mathcal{N} = N \text{ or } N - 1. \quad (1)$$

The additional parameter ξ is a *weight* that will be assigned to the ionized state in the following. The local potential $v^{\lambda,\xi}(\mathbf{r})$ is adjusted such that the so-called ensemble density $n^{\lambda,\xi}(\mathbf{r})$, which is a weighted sum of neutral and ionized densities, **does not vary with ξ and λ** :

$$n^{\lambda,\xi}(\mathbf{r}) = \left[1 - \frac{(N-1)\xi}{N} \right] \times n_{\Psi_N^{\lambda,\xi}}(\mathbf{r}) + \xi \times n_{\Psi_{N-1}^{\lambda,\xi}}(\mathbf{r}) = n(\mathbf{r}) \quad \forall \lambda, \forall \xi. \quad (2)$$

- a) [1 pt] Verify that, by construction, the ensemble density integrates to the number N of electrons in the neutral system: $\int d\mathbf{r} n^{\lambda,\xi}(\mathbf{r}) = N$.
- b) [2 pts] Let us consider the $\xi = 0$ limit of the theory. How would you name the local potentials $v^{\lambda=1,\xi=0}(\mathbf{r})$ and $v^{\lambda=0,\xi=0}(\mathbf{r})$? Are they uniquely defined by the density constraint in Eq. (2)?
- c) [0.5 pt] We introduce the following density functionals,

$$\begin{aligned} F^{\lambda,\xi}[n] &= \left[1 - \frac{(N-1)\xi}{N}\right] \times \langle \Psi_N^{\lambda,\xi} | \hat{T} + \lambda \hat{W}_{\text{ee}} | \Psi_N^{\lambda,\xi} \rangle + \xi \times \langle \Psi_{N-1}^{\lambda,\xi} | \hat{T} + \lambda \hat{W}_{\text{ee}} | \Psi_{N-1}^{\lambda,\xi} \rangle, \\ E_{\text{Hxc}}^{\xi}[n] &= F^{\lambda=1,\xi}[n] - F^{\lambda=0,\xi}[n]. \end{aligned} \quad (3)$$

Are they universal?

- d) [2 pts] Show that conventional (N -electron) KS-DFT is recovered from Eqs. (2) and (3) when $\xi = 0$. How would you name the functionals $F^{\lambda=1,\xi=0}[n]$, $F^{\lambda=0,\xi=0}[n]$, and $E_{\text{Hxc}}^{\xi=0}[n]$? Which energy contributions do they describe?
- e) [2 pts] Deduce from Eqs. (1) and (2) that $F^{\lambda,\xi}[n] = \left[1 - \frac{(N-1)\xi}{N}\right] \times E_N^{\lambda,\xi} + \xi \times E_{N-1}^{\lambda,\xi} - \int d\mathbf{r} v^{\lambda,\xi}(\mathbf{r})n(\mathbf{r})$.
- f) [1.5 pts] Prove that $\frac{\partial E_{\mathcal{N}}^{\lambda,\xi}}{\partial \xi} = \int d\mathbf{r} \frac{\partial v^{\lambda,\xi}(\mathbf{r})}{\partial \xi} n_{\Psi_{\mathcal{N}}^{\lambda,\xi}}(\mathbf{r})$ where $\mathcal{N} = N$ or $N-1$. **Hint:** prove the Hellmann-Feynman theorem, $\frac{\partial E_{\mathcal{N}}^{\lambda,\xi}}{\partial \xi} = \left\langle \Psi_{\mathcal{N}}^{\lambda,\xi} \left| \frac{\partial \hat{H}^{\lambda,\xi}}{\partial \xi} \right| \Psi_{\mathcal{N}}^{\lambda,\xi} \right\rangle$ where $\hat{H}^{\lambda,\xi} = \hat{T} + \lambda \hat{W}_{\text{ee}} + \sum_{i=1}^{\mathcal{N}} v^{\lambda,\xi}(\mathbf{r}_i)$, and conclude.
- g) [1.5 pts] Deduce from Eq. (2) and questions 2. e) and 2. f) that $\frac{\partial F^{\lambda,\xi}[n]}{\partial \xi} = E_{N-1}^{\lambda,\xi} - \frac{(N-1)}{N} \times E_N^{\lambda,\xi}$.
- h) [1 pt] Let $I_N = E_{N-1}^{\lambda=1,\xi=0} - E_N^{\lambda=1,\xi=0}$ denote the exact ionization potential of a given N -electron system. We denote ε_N the HOMO energy (where HOMO stands for *highest occupied molecular orbital*) that would be obtained by applying standard KS-DFT to the latter system. Explain why $\varepsilon_N = -\left(E_{N-1}^{\lambda=0,\xi=0} - E_N^{\lambda=0,\xi=0}\right)$.
- i) [1.5 pts] Let $C_N = \frac{1}{N} \left(E_N^{\lambda=1,\xi=0} - E_N^{\lambda=0,\xi=0}\right)$. Is C_N expected to be equal to zero in the exact theory? Justify your answer by considering the exact (interacting) energy decomposition used in KS-DFT.
- j) [1.5 pts] Deduce from Eq. (3) and questions 2. g), 2. h), and 2. i) that $I_N = -\varepsilon_N - C_N + \left. \frac{\partial E_{\text{Hxc}}^{\xi}[n]}{\partial \xi} \right|_{\xi=0}$.
- k) [1.5 pts] The following fundamental question naturally arises in KS-DFT: *Can we interpret the energy of the HOMO as minus the ionization potential of the true (interacting) system under study?* Explain why this question is of primary importance, for example, in the field of nanotechnology, and bring an answer in the light of question 2. j).